

Bio-dissolution of spent nickel–cadmium batteries using *Thiobacillus ferrooxidans*

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Abstract

In this study, the production of sulphuric acid in bioreactors with *Thiobacillus ferrooxidans* attached on elemental sulphur was investigated. These bioreactors reached a maximum H^+ productivity of $80 \text{ mmol kg}^{-1} \text{ d}^{-1}$ of support. This medium was used for the indirect dissolution of spent nickel–cadmium batteries recovering after 93 days 100% of cadmium, 96.5% of nickel and 95.0% of iron. Moreover, recoveries higher than 90.0% were reached when anodic and cathodic materials were directly added to *Thiobacillus ferrooxidans* cultures with sulphur as the sole energy source. The results presented show an economic and effective method which could be considered the first step to recycle spent and discarded batteries preventing one of the many problems of environmental pollution. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Nickel–cadmium batteries; Environmental pollution; *Thiobacillus ferrooxidans*; Bioleaching

1. Introduction

In Argentina, nickel–cadmium batteries are still used extensively in mobile telephones, as in other varieties of applications, but no technology is being implemented for their recovery in this country. More than a million of nickel–cadmium batteries are discarded every year in our country after

using in mobile telephones. Nickel–cadmium batteries are classified as hazardous waste because nickel and cadmium are heavy metals and suspected carcinogens (Shapek, 1995). That is why it is desirable to find an economic and environmentally friendly process to recycle these batteries allowing the recovery of the valuable elements contained.

In other places of the world, there are some methods to treat spent batteries (de Juan et al., 1995, 1996) involving pyro and hydrometallurgi-

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cal techniques similar to those used in mining the industry. The methods that involve pyrolysis are fast and efficient but quite expensive and they usually produce polluting emissions; on the other hand, the hydrometallurgical methods, while cheaper and less polluting, are usually not as efficient. In the mining industry, the biohydrometallurgical processes have been gradually replacing the hydrometallurgical ones due to their higher efficiency, lower costs and few industrial requirements (Ehrlich, 1981; Bosecker, 1986; McNulty and Thompson, 1990; Rossi, 1990; Jain and Tyagi, 1992; Barrett et al., 1993). In the same way, biohydrometallurgy could be a sound alternative for the recycling of valuable elements in nickel–cadmium batteries in the countries where the technology needed for this process has not been developed yet and the environmental protection policy is becoming gradually more strict.

Possibly, the main biohydrometallurgical process is the bacterial leaching of sulphide ores. One of the most important mesophiles involved in this process is *Thiobacillus ferrooxidans*, which obtains energy from the aerobic oxidation of either iron(II) or reduced sulphur compounds. Therefore, enhanced leaching of sulphide ores by *T. ferrooxidans* may occur in two ways: direct and indirect. The indirect mechanism entails the oxidation of the sulphides by the iron(III) produced by bacterial oxidation of iron(II) and the direct mechanism is produced by a frontal attack on the sulphide by the bacteria (Ehrlich, 1981; Donati et al., 1988, 1996).

Moreover, *T. ferrooxidans* can grow using elemental sulphur as energy source with oxygen as the last electron acceptor. The oxidation of sulphur generates a series of sulphur compounds (sulphite and thiosulphate among others) with high reducing power and sulphuric acid as the last product (Sisti et al., 1996).

On the other hand, remarkable tolerance to many toxic metals (as nickel and cadmium) at high concentrations can be developed by some strains of *T. ferrooxidans*. This tolerance is essential when using contact leaching systems. However, in the last years, attached bacteria systems (Lancey and Tuovinen, 1984; Grishin and Tuovinen, 1988; Garcia et al., 1989; Porro et al.,

1993) have been developed as an alternative to contact leaching process allowing the bioleaching parameters (aeration, pH, toxicity level of metallic ions) to be easily controlled.

These systems (biofilm reactors) have been used to produce iron(III) (as leaching medium) more quickly and continually due to the high bacterial concentration on the surface of an inert or active support. In other cases, biofilm reactors with *T. ferrooxidans* or *T. thiooxidans* on elemental sulphur have been used to reach high sulphuric acid productivity (Curutchet et al., 1996; Pogliani et al., 1997).

As regards the nickel–cadmium batteries, the cells are available in different configurations, but the most popular are the cylindrical cells. Cylindrical cells are sealed and contained within a nickel plated steel container (negative terminal) which is separated from the cover (positive terminal) by a polypropylene ring (an insulator). A grid structure which acts to hold active materials is usually made of nickel steel. On this grid, a porous structure of nickel foam may be bonded or sintered generating a framework. The active materials are pasted, chemically or electrochemically deposited or vacuum deposited onto this framework. Nickel oxyhydroxide (NiOOH) is the cathodic active material which is converted to nickel hydroxide (Ni(OH)_2) during the discharge of the battery. The anodic active material contains cadmium metal which is converted to cadmium hydroxide (Cd(OH)_2) on the discharge. Enough solution of potassium hydroxide to wet internal cell components is added as an electrolyte.

The described components of the nickel–cadmium batteries (essentially hydroxides and easily oxidised metals) can be dissolved by the sulphuric acid generated by *T. ferrooxidans*. Sulphuric acid is a strong acid and a moderately oxidising agent capable of oxidising metals such as nickel, cadmium and iron (Cotton and Wilkinson, 1988) as well as other mineral dilute acids. Additionally, the intermediates generated during the bio-oxidation of sulphur (see above) could contribute to the dissolution of nickel oxyhydroxide by prior reduction to nickel(II) (more soluble than nickel oxyhydroxide in acid solution).

The purpose of this article is to present the results of the experiments using *T. ferrooxidans* culture with sulphur as energy source to dissolve nickel–cadmium batteries and to neutralise its electrolyte. Because of its low costs, this process could be the first step in the treatment of nickel–cadmium batteries before recovering metals by physicochemical methodologies. Preliminary experiments of dissolution were carried out in shake flasks to evaluate the feasibility of a contact leaching process in which the *T. ferrooxidans* strain used was previously adapted to high concentrations of nickel and cadmium. Taking into account the obtained results and with the purpose of analysing the advantages of an indirect bioleaching process (probably more suited for a commercial application), two percolators were arranged in series. *T. ferrooxidans* immobilised on elemental sulphur in the first percolator produced acidic growth medium which was used in the second percolator for the extraction of nickel and cadmium from a spent battery.

2. Materials and methods

2.1. Bacteria

A *T. ferrooxidans* strain from Santa Rosa de Arequipa-Perú (DSM 11477) was used. The organism was propagated in an iron-free 9 K medium (Silverman and Lundgren, 1959) at initial pH of 2.0 with powdered sulphur (10 g l^{-1}) as energy source. Bacteria were harvested at culture pH about 1.0, resuspended with iron-free 9 K medium (pH = 4.0) and used as inocula in the different experiments.

2.2. Resistant strains

Inhibition of *T. ferrooxidans* growth cultures on sulphur was investigated with addition of NiSO_4 or CdSO_4 (between 0.050 and 2.0 g l^{-1} of nickel(II) or cadmium(II)) at 30°C and 180 rpm . The rates of acid production were compared to a control (culture without toxic metals) after 11 days. Bacteria from the cultures with the highest concentration of metal that produced acid at the

same speed as the control (2.0 g l^{-1} for nickel and 0.50 g l^{-1} for cadmium) were used as inocula for the adaptation experiments.

Both cadmium-resistant and nickel-resistant strains were obtained by serial subcultures in a medium with sulphur as the sole energy source with increasing concentrations of nickel (from 2.0 g l^{-1} up to 18 g l^{-1}) added as NiSO_4 and cadmium (from 0.50 g l^{-1} up to 10 g l^{-1}) added as CdSO_4 . These experiments were carried out in shake flasks at 30°C and 180 rpm . It was considered that bacteria was resistant to a metal cation, at a given concentration, when the pH reached the value 1.0 after 3 or 4 days (similar to the control without nickel or cadmium) and free bacterial population was at least $5 \times 10^8 \text{ cells ml}^{-1}$. In this case, an inoculum of the subculture was transferred to a fresh medium with higher metal concentration.

2.3. Bio-dissolution of cathodic and anodic materials in batch cultures

Erlenmeyer flasks containing 100 ml of an iron-free 9 K medium (initial pH was adjusted to 4.0) with an initial bacterial population of $5 \times 10^7 \text{ cells ml}^{-1}$ were incubated at 30°C and 180 rpm . Additionally, 1 g of analytical grade powdered sulphur was added as the sole energy source.

Active materials were separated manually from spent-cylindrical broken cells and cut up to obtain different portions. Cathodic and anodic materials contained 56.8% of nickel and 57.5% of cadmium, respectively. It was not possible to obtain homogeneous portions of anodic material smaller than 0.10 g . When pH reached a value of about 1.0, anodic material (0.10 , 0.15 and 0.20 g) or cathodic material (0.050 , 0.10 , 0.15 and 0.20 g) coming from a spent broken cell was added to the flasks. The active materials were not added at the beginning to avoid a fast increase of pH that would inhibit bacterial growth (data not shown).

Sterile controls for each amount of active material were performed in absence of bacteria using filter-sterilised medium at initial pH of 4.0 with 10 g l^{-1} of sulphur. Similar sterile controls with filter-sterilised sulphuric acid at initial pH of 1.0 for the maximum pulp density (0.20 g l^{-1}) were carried out.

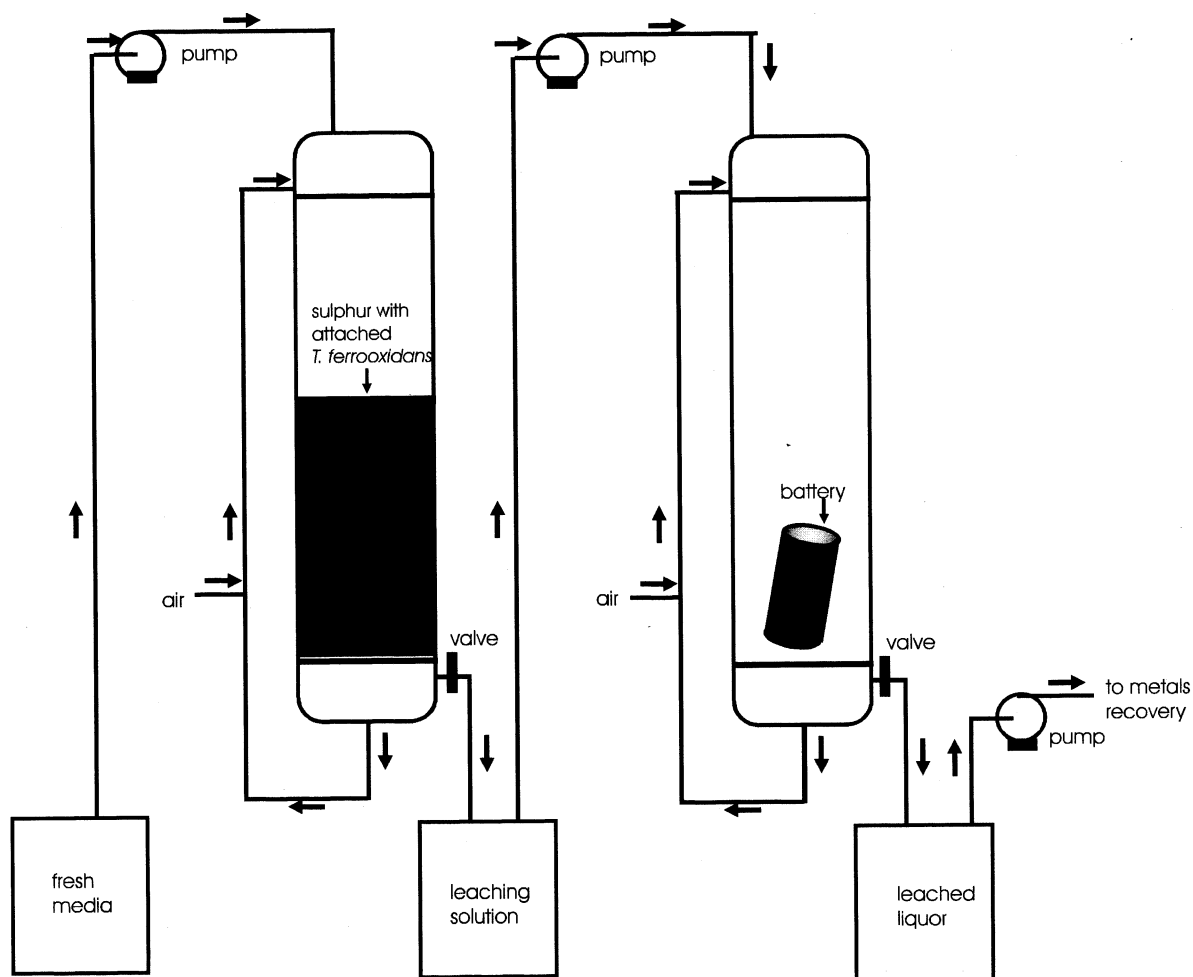


Fig. 1. A schematic representation of the two percolators system used for the dissolution of a spent nickel–cadmium battery.

2.4. Bio-dissolution of nickel–cadmium batteries in a two percolators system

The experiments were carried out using a system similar to Fig. 1. The system consisted in two percolators placed in series. The first percolator was a sulphuric acid bioreactor with *T. ferrooxidans* immobilised on elemental sulphur. The acidic medium produced in the first percolator was pumped to the second percolation column which contained a whole spent battery previously broken.

The mean weight of the spent cells used in these experiments was 24.9 g and they contained 18.8%

of nickel, 20.4% of iron, 23.5% of cadmium and 6.6% of plastic components.

The first percolator (sulphuric acid producing bioreactor) was prepared as follows: 160 g of elemental sulphur (particle size: about 2–4 mm) were added to a percolation column. A flow of 120 l h^{-1} air was continually fed to the solution. A total of 180 ml of an iron-free 9 K medium (initial pH = 2.0) were added to the column and inoculated with 20 ml of *T. ferrooxidans* culture in an exponential stage of growth. The system was maintained at 30°C. When the pH value was between 0.7–1.0, all the exhausted medium was replaced by the same volume of a fresh medium

(without new inoculation). The procedure was repeated until a constant rate of sulphuric acid production was reached (this situation indicates the maximum attached bacterial population). Later, the bioreactor produced sulphuric acid continually and at a constant rate.

The battery was placed in the percolation column and media produced in the *T. ferrooxidans* bioreactor (pH about 1.0) were added. The media were previously filtered through medium fast speed filter-paper to eliminate elemental sulphur but not colloidal sulphur or suspended cells. The liquid phase in the column was pumped to the top of the percolation column by air pressure. When the pH was too high (higher than 2.5) or metal concentrations in the solution did not change, all the medium was replaced by fresh medium in order to continue metal dissolution (see below). This procedure was repeated nine times during the experience which lasted 93 days.

2.5. Analytical determinations

Soluble cadmium, nickel and iron were determined by atomic absorption spectrophotometry. The sulphuric acid formed was analysed by titration with sodium hydroxide solution with phenolphthalein as acid-base indicator. Because sulphuric acid is produced when *T. ferrooxidans* uses sulphur as an energy source for autotrophic growth, sulphuric acid production was correlated with bacterial growth (Rossi, 1990). Suspended bacterial populations were determined by direct counting using a Petroff–Hausser type cell counter in a microscope with a phase contrast attachment. Assuming there is a close correlation between the evolution of both suspended and total bacterial populations (see Escobar et al., 1996), suspended bacterial populations were used to check bacterial growth.

3. Results

3.1. Acclimation of *T. ferrooxidans* to nickel and cadmium

The sulphuric acid production by cultures of *T.*

ferrooxidans on elemental sulphur was not inhibited at nickel(II) concentrations between 0.050 and 2.0 g l⁻¹ because this production proceeded at a similar rate as the one of the control in the absence of nickel. On the other hand, cadmium(II) was more toxic than nickel, producing lag phases (96 h or more for concentrations higher than 1.0 g l⁻¹). The inhibition of the sulphuric acid production was calculated as the ratio between acid production in each culture and the control (without inhibitor) after 11 days; the values obtained were 73 and 68% for cultures with 1.0 and 2.0 g l⁻¹ of cadmium(II), respectively. No cell growth was detected within 11 days when cadmium concentrations were higher than 3 g l⁻¹.

Fig. 2 illustrates the development of Ni-resistant and Cd-resistant strains of *T. ferrooxidans* growing on elemental sulphur. Each data point corresponds to the time the culture took to reach a suspended bacterial population at least of 5 × 10⁸ cells ml⁻¹ and a pH equal to or lower than 1.0 within 3 or 4 days. This behaviour (similar to the control without nickel or cadmium) was considered as adequate growth.

In agreement with the higher sensitivity, *T. ferrooxidans* adaptation to cadmium(II) requires

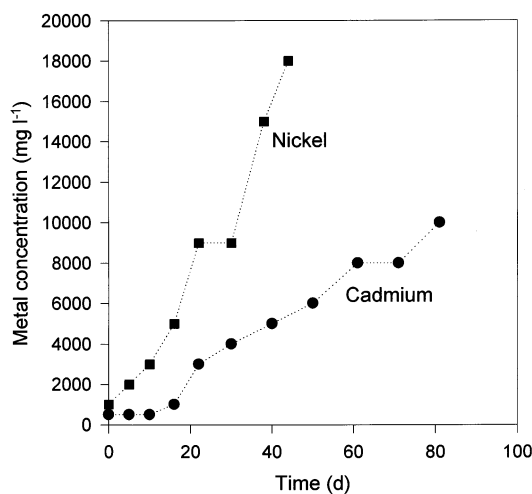


Fig. 2. *Thiobacillus ferrooxidans* adaptation to nickel(II) and cadmium(II) growing on elemental sulphur. Each point indicates the time the culture took to reach an adequate bacterial growth (see text).

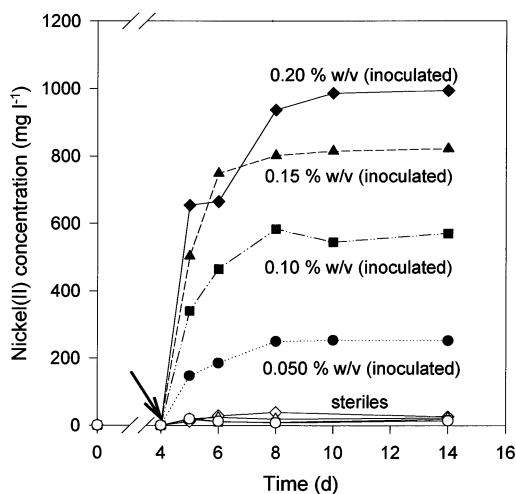


Fig. 3. Nickel(II) concentration during the bioleaching of cathodic material (obtained from a spent nickel–cadmium battery) at four different pulp densities by *Thiobacillus ferrooxidans* growing on elemental sulphur. Sterile systems are indicated by hollow symbols (similar to the corresponding filled symbols). The arrow indicates when active materials were added to the cultures.

more time than to nickel(II) (Norris and Kelly, 1978). It could be possible to reach higher metal concentrations, but it was not done because in the contact experiments described in this paper the metal concentrations were always lower than 2.0 g l⁻¹.

3.2. Bio-dissolution of cathodic and anodic materials in batch cultures

Fig. 3 illustrates the pattern for metal concentration during the bioleaching of the cathodic material (contained 56.8% of nickel) for four different pulp densities (% w/v of active material to medium volume). The active materials were added to the cultures when it reached a pH of 1.0 (indicated by an arrow in the figure). When active materials were added at a higher pH, the high basicity of those substances inhibited the bacterial growth (data not shown). The percentages of extraction of nickel were 87.5, 96.4, 100.0 and 88.7% for 0.20, 0.15, 0.10 and 0.050 g of active material added to a culture.

As it can be seen, the nickel extraction in the sterile systems (at initial pH of 4.0) was negligible

(between 2.0 and 5.0% for the different pulp densities). These results are in agreement with the rapid increase of pH (between 6.2 and 7.1) after adding the active materials preventing the acid dissolution. In other sterile experiments (data not shown) with sulphuric acid at initial pH of 1.0, after 20 days the nickel released was 20% from 0.20% p/v of cathodic material.

Although the cathode did not contain cadmium, this metal must have been attached to the cathodic material when the different components of the battery were separated since it was found in the bioleaching of cathodic material. As soon as the cathodic material was added to the cultures, cadmium concentration reached its maximum value. The cadmium concentrations were 70.8, 55.5, 43.2 and 19.5 ppm for 0.20, 0.15, 0.10 and 0.050% p/v respectively.

Cadmium(II) concentration in the bioleaching of the anodic material (contained 57.5% of cadmium) is shown in Fig. 4. In this case, nickel was not found in the leaching media. The percentages of cadmium extraction were 84.6, 95.8 and 91.8% for 0.20, 0.15 and 0.10% p/v. In the sterile systems the pH stabilised at about 6.3–6.7 (for the differ-

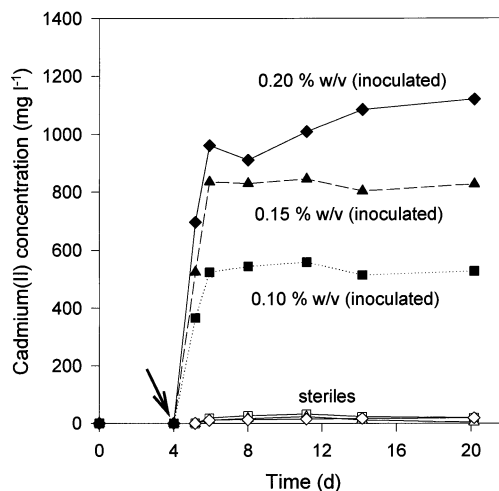


Fig. 4. Cadmium(II) concentration during the bioleaching of anodic material (obtained from a spent nickel–cadmium battery) at three different pulp densities by *Thiobacillus ferrooxidans* growing on elemental sulphur. Sterile systems are indicated by hollow symbols (similar to the corresponding filled symbols). The arrow indicates when active materials were added to the cultures.

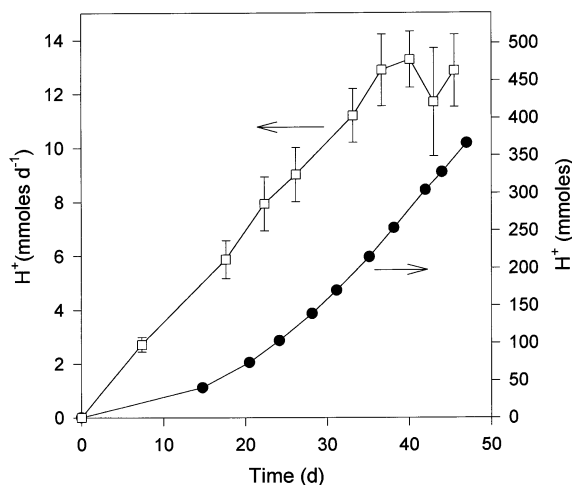


Fig. 5. Mean productivity and cumulative production of sulphuric acid in a bioreactor with *Thiobacillus ferrooxidans* immobilised on elemental sulphur.

ent pulp densities) as the extractions were lower than 3%. In other sterile experiments (data not shown) with sulphuric acid at initial pH of 1.0, after 20 days the cadmium extraction was 55% for 0.20% p/v of anodic material.

3.3. Bio-dissolution of nickel–cadmium batteries in a two percolators system

Fig. 5 indicates the mean productivity and cumulative production of sulphuric acid obtained in the *T. ferrooxidans* bioreactor. As it can be seen, the productivity increased to a maximum value after 35 days (13 mmol d^{-1}). This sulphuric acid productivity (probably correlated to a maximum attached bacterial population) was approximately constant (data not shown) until the end of the experiment (more than 100 days).

Fig. 6 represents the metal concentrations reached during each step of extraction with a leaching medium (there were nine steps using 300 ml of fresh medium in each case) previously generated in the bioreactor. The medium was in contact with the battery for different times before replacing it with a new medium: 12.3, 11.3, 124.4, 153.0, 219.0, 297.3, 602.7, 736.0 and 72.0 h, respectively, for each successive step. The whole experiment continued for 93 days.

The replacement of the medium on the first, second and fourth steps was done when the pH was higher than 1.80 (2.3, 2.1 and 1.9 respectively) preventing the metal precipitation as hydroxides (for these metals hydroxides still precipitate at low pH). The replacement of medium on the other steps was performed when stabilisation of metals concentration in solution was reached (in these cases pH was lower than 1.5).

When the metal concentrations were stabilised on the last step, the experiment was stopped because the amount of metals recovered until then was higher than the mean content of these metals in the nickel–cadmium batteries (see Section 2). The composition of the leach residue (7.8% of initial mass) was determined by the treatment of filtered solids with 6 N hydrochloric acid solution. Iron and nickel but not cadmium were released by the residue, therefore the percentages of extraction after 93 days were 100% of cadmium, 95.0% of iron and 96.5% of nickel.

4. Discussion

The dissolution of cathodic material in the cultures of *T. ferrooxidans* was slow (it took more

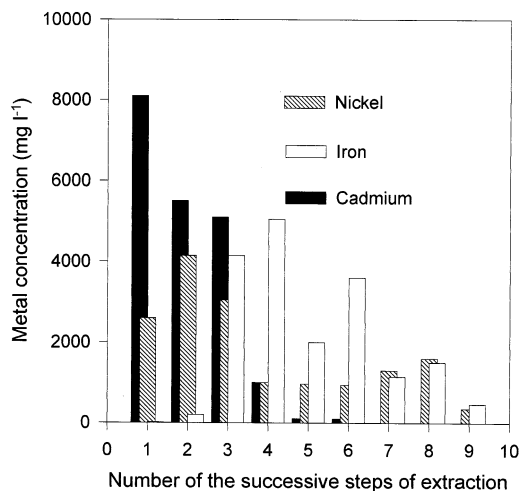


Fig. 6. Metal released during the steps of the indirect bioleaching of a spent nickel–cadmium battery using media produced in a bioreactor with *Thiobacillus ferrooxidans* immobilised on elemental sulphur

than 72 h). An increase of pulp density (higher amount of material) resulted in a higher consumption of medium for its total dissolution and consequently more time of bio-oxidation of sulphur.

According to the higher solubility of cadmium hydroxide than nickel hydroxide and the higher reducing power of cadmium than nickel (i.e. elemental cadmium is easier oxidised than elemental nickel), the attack of anodic material by *T. ferrooxidans* was faster than that corresponding to cathodic material. The maximum dissolution was reached after approximately 18 h for the different pulp densities.

The increase and later decrease of the percentage of metal dissolution in the cultures with the increase of the pulp density remains unclear. However, it is possible to conclude that the increase in the dissolution, due to the higher exposed surface, could be compensated by a bigger number of attached bacteria on the active material which is not an energy source for *T. ferrooxidans*. Because of the high bacterial population attached to this material, a lower bacterial population could attach to sulphur and catalyse its oxidation producing leaching medium (Curutchet et al., 1990).

The results obtained in the controls with sulphuric acid at pH of 1.0 were significantly lower than the ones obtained with the inoculated systems. This shows that there are at least two indirect mechanisms of *T. ferrooxidans* action: (1) an acid and a moderately oxidising attack by sulphuric acid similar to the one obtained in the control with sterilised sulphuric acid; and (2) a second attack by intermediate reducing compounds which allows a higher dissolution of nickel oxyhydroxide (Steudel et al., 1987; Sisti et al., 1996).

In the bioreactor, the maximum productivity was reached a long time because the support surface was increased by bacterial action. This is why the sulphur crystals are first converted to colloidal sulphur which is able to enter the periplasmic space of cells (Karavaiko et al., 1988). When the bioreactor reached a constant production rate, it could produce about $80 \text{ mmol H}^+ \text{ kg}^{-1} \text{ d}^{-1}$ which was calculated assuming a linear dependence between the amount of support and

productivity. Although the productivity was calculated by direct extrapolation of the experimental rate of acid production, it obviously depends on the details of the bioreactor, the surface sulphur exposed (which is in a relationship with the particle size), the population of attached cells, the uniform contact between liquid and solid and the availability of oxygen, among others.

The metal dissolution had a similar behaviour in both experiments (in shake flasks and in a two percolators system) with high release of cadmium during the first steps. Nickel and iron were released more slowly than cadmium. The rapid dissolution of cadmium and nickel and a fast increase of pH in the two first steps indicate a relationship between both of them (it was an acid dissolution). It was noted that during the following steps of extraction, the rates of dissolution were lower with no significant increase in pH. This could indicate the first dissolution of the oxidised species (oxides and hydroxides) and the neutralisation of the electrolyte (KOH) and a later dissolution of species as elemental metals (especially iron and nickel) which are slowly oxidised by sulphuric acid at the pH of these experiments.

After the fourth step, there was no relationship between the metal release and the pH because there was no significant change in pH, although the dissolution of hydroxides or metal oxidation should consume acid and increase the pH. This implies that there was a later production of sulphuric acid in the column with the battery. This could have been due to the presence of *T. ferrooxidans* attached to colloidal sulphur in the media taken from the first column. The presence of viable cells in the media in the second column was confirmed by transferring an aliquot to a sterile ferrous medium; iron was oxidised much faster than the corresponding sterile control and the microscope observations revealed bacterial growth.

The almost total dissolution of nickel from the battery shows not only the oxidation of metallic nickel and the dissolution of nickel hydroxide but also the reduction and further dissolution of nickel oxyhydroxide. The reduction of the last compound is only possible in the second column through the action of intermediate reducing com-

pounds of sulphur metabolism. These compounds probably reached the second column attached to the surface of colloidal sulphur, since they were not detected in the filtered solution (through a 0.22 μm pore size) by measurement of the absorbance at 222 nm (Steudel et al., 1987; Shirohara et al., 1993).

Owing to the confirmation of the presence of viable cells, the medium in the column was changed when the metal concentrations did not increase significantly in the solution. It prevented the possible iron(II) oxidation by *T. ferrooxidans*. Although *T. ferrooxidans* grown on elemental sulphur shows a longer lag phase when it is inoculated on iron(II) (Kulpa et al., 1986; Donati et al., 1996), finally iron(II) is completely oxidised at a pH higher than 1.2 (at pH lower than 1.2 the bacterial oxidation of iron(II) is completely inhibited) (Sand, 1989). Iron(III) production and the consequent increase of pH would produce jarosite (iron(III) basic sulphates) (Tuovinen and Carlson, 1979; Curutchet et al., 1992) when pH was a bit higher than 1.5. Simultaneously nickel, cadmium and iron could co-precipitate so the jarosite precipitation should be prevented.

The total release of iron, nickel and cadmium contained in a spent battery required about 2.5 l of medium generated in the bioreactor. This implies a consumption of 250 mmol H^+ for one battery although only in the first, second and fourth extractions was there a large acid consumption while in the rest of the extractions the media still presented a high acid concentration (pH was not increased significantly).

The maximum productivity of the sulphuric acid (80 mmol H^+ $\text{kg}^{-1} \text{d}^{-1}$) is equivalent to 0.8 l of medium of pH 1.0 per day and kg of elemental sulphur. Thus, this bioreactor containing 1 kg of sulphur and working at its maximum rate for 3 days could produce the medium necessary to leach a whole spent battery. Moreover according to the balanced equation, a bioreactor like that could produce (prior to the exhaustion of the sulphur) more than 600 l of medium of pH 1.0 (about 60 mmol H^+ for kg of sulphur) enough to leach more than 240 nickel–cadmium batteries.

The present studies showed that the *T. ferrooxidans* cultures on elemental sulphur could be used

through the production of sulphuric acid and reducing-power compounds, to leach 'in situ' or indirectly a whole spent battery or their active materials. The results obtained in the 'in situ' methodology could imply that it would be possible to use *T. ferrooxidans* to leach spent nickel–cadmium batteries because of the high metal extraction and the possibility to obtain of a Cd-resistant strain and a Ni-resistant strain. However, the separation of active materials of the batteries container and the use of shake flasks are not an adequate methodology for an industrial process. Besides the metals, recovery from the active materials was high but not complete. On the other hand, the dissolution of whole broken batteries using immobilised bacteria on a support (which was also the substrate) could be a valuable process to recycle spent nickel–cadmium batteries which could be industrially applied. Moreover, in this case it is not necessary to use resistant strains and the metals recovery was almost complete.

Even though a comparative economic estimate has not been done, in a very rough cost calculation, bacterial acid production seems to be cheaper than the direct use of sulphuric acid. In similar bioleaching process (of non-sulphide industrial waste products and residual sludge from sewage treatment plants) it has been estimated that taking into account only the costs of chemicals, the biotechnology method is 70–80% cheaper than the chemical methodology (Bosecker, 1986; Jain and Tyagi, 1992). Furthermore, the biotechnology route has the following advantages: lower operational difficulties including the fact of elemental sulphur required in this process is easy to store and transport, unlike the acid-requiring process. On the other hand, the chemical methodology requires acid-corrosion resistant apparatus and safe storage and transportation facilities for concentrate acid and its costs of transport are higher.

Summarising, it may be concluded that this biotechnology process shows greater possibilities of being the first step (more effective and more economic than direct process with sulphuric acid) to the recycling of spent nickel–cadmium batteries preventing the contamination generated by discarded batteries and allowing the recovery of metals contained inside the batteries.

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